



PCT/GB2004/001353

Rec'd PCT/PTO 03 OCT 2005

10/551774

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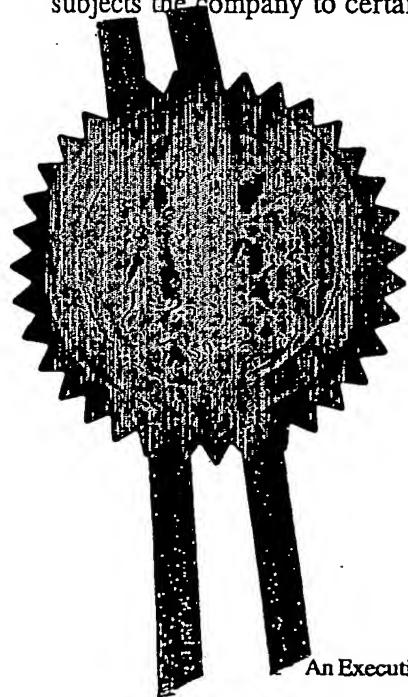
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07APR03 E798042-1 D00192  
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1. Your reference

N 88299 TAC/JAT

2. Patent application number

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= 4 APR 2003

0307890.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Silberline Limited  
Banbeath Road  
Leven  
Fife KY8 5HD

721464001

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

UNIVERSAL DISPERSIONS  
METAL PIGMENT COMPOSITION

5. Name of your agent (if you have one)

J.A. KEMP &amp; CO.

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

14 South Square  
Gray's Inn  
London  
WC1R 5JJ

26001

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Country      Priority application number  
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- b) there is an inventor who is not named as an applicant, or
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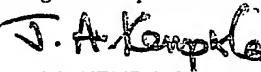
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Signature  Date 4 April 2003  
J.A. KEMP & CO.

12. Name and daytime telephone number of person to contact in the United Kingdom

T.A. CRESSWELL  
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## METAL PIGMENT COMPOSITION

5

The present invention relates to a process for preparing low- or non-dusting, substantially non-volatile metal pigment compositions by a milling process using a non-hydrocarbon milling fluid.

10 The preparation of metal flake pigments is well documented in the patent literature. Metal flakes can be prepared in the complete absence of solvent by a dry ball milling process, but this can be hazardous in the case of reactive metals such as the widely employed aluminium, due to the contaminating and/or explosive properties of the dry flake products.

15

Wet ball milling processes are also known in which metal powder or chopped foil is milled with an organic liquid such as mineral spirits and a small amount of a lubricant. However, the solvent portion of such metal pigment pastes is especially disadvantageous in printed films on packaging intended for food contact and the presence of organic solvent can also cause bubbles and surface blemishes in the pigmented plastic articles. It is also found that the storage stability of metal pigment pastes themselves is limited, due to the tendency of the organic solvent component to evaporate, leading to aggregation of the metal flake particles.

25

Environmental concern over volatile organic solvents in industrial processes has led to pressure for their elimination from metal flake pigment manufacturing processes and products and requires expensive equipment for solvent capture.

30 The need for a stable, safe and easily handled metal pigment product form has been met by the products of European Patent 0134676. There is described

therein a process for the preparation of a solid, low- or non-dusting, metal pigment composition, which comprises forming a coherent paste of an organic binder medium, an organic liquid vehicle and metal pigment, in powder or flake form. The coherent paste is either sub-divided into particles and substantially all  
5 the organic liquid removed, or substantially all the organic liquid vehicle is removed from the coherent paste and the resulting mass sub-divided into particles.

The problem of metal flake dusting may be reduced if the metal powder precursor  
10 is milled in the presence of a suitable organic carrier material. However, methods traditionally used to separate wanted from unwanted particle size fractions, such as dilution with solvent, followed by wet screening, are then no longer operable at the dilutions necessary for efficient separation.

15 At first sight, water appears to be a more satisfactory processing liquid. It is readily available, inexpensive and non-flammable. However, a difficulty arises in the case of the more reactive metal pigments, especially aluminium, which is the most widely used of such pigments. Finely divided aluminium metal may react with water to form aluminium oxide and hydrogen gas and the pigmentary  
20 properties of the metal flake are destroyed.

In European Patent -A-0934365 there is described the milling of aluminium powder in a milling fluid consisting substantially of water, in the presence of one or more additives, which together exhibit lubricating, corrosion inhibiting and  
25 surfactant properties. The milled material is subsequently converted into a low-or non-dusting, substantially non-volatile, metal flake pigment composition. However, the unpredictability of the aluminium reaction with water means that product integrity cannot always be guaranteed. There therefore remains a need for a fully satisfactory, commercially viable process that can be used to prepare  
30 aluminium and other metal pigments in the substantial absence of both water and hydrocarbon solvents, whilst affording appropriate covering power, opacity, gloss

and other desirable properties of metal flake pigments and preserving stability of the product.

Thus, according to the present invention, there is provided a process for 5 preparing a low volatility metal flake pigment composition, which comprises milling metal powder in a non-aqueous, non-hydrocarbon milling fluid, optionally in the presence of one or more substances that act as a lubricant and/or corrosion inhibitor. By non-hydrocarbon is meant an organic liquid that contains elements such as oxygen or nitrogen, in addition to hydrogen and carbon.

10

After milling, unwanted oversize or undersize particles may be removed, for example by screening, before the metal pigment slurry is concentrated to a metal flake pigment paste of typically 50 to 90% metal by weight. Such a paste may be sold as prepared, or may desirably be converted into a non-dusting, easily 15 meterable granule form (also known as pellets).

To prepare the latter, an organic binder may be incorporated in the metal pigment paste by mixing, optionally at elevated temperature, to form a coherent paste of organic binder, milling fluid and metal flake pigment. The paste, which typically 20 contains from 3 to 70% of organic binder, based on the weight of the metal flake, may be sub-divided into particles, at least 98% by weight of the resulting particles being retained on a sieve having a 150 $\mu\text{m}$  aperture and each containing a plurality of metal pigment particles dispersed and bound in a matrix of organic binder and milling fluid.

25

There is a considerable commercial advantage through reduced stockholding if one product can be employed satisfactorily in both solvent-based and water-based coatings and potentially also in mass-pigmented plastics. Such a metal flake pigment product is obtained if a milling liquid is used that is not only both 30 solvent and water miscible, but acts as a plasticiser in plastics. Such liquids are desirably also of low toxicity and odour, but also substantially non-volatile at

ambient temperature, thereby limiting losses to atmosphere during manufacture, storage and use. Aggregation of metal flakes, due to solvent loss by evaporation, which causes reduced aesthetic performance, is also thereby avoided. Low volatility extends to the application. For example, in inks or paints, the milling liquid is substantially retained in the coating, rather than being lost to atmosphere in the conventional drying of such coatings.

Another advantage of the process of the present invention is the ability to treat the milled flakes whilst in the milling fluid. This may be for a variety of purposes. For example, during milling, the developing flakes may optionally be treated with ammonium dichromate, or coated with silica or alumina, to improve stability in aqueous application media. Other treatments, such as with ammonium or potassium permanganate, may be used to provide coloration of the flake surface, for example to simulate gold. Still further treatments may improve the hardness and therefore the shear resistance of such flakes in application media.

It is a further advantage of the process of the invention that water is substantially eliminated from contact and potential reaction with the metal pigment during preparation, through the formation of the substantially non-volatile metal pigment composition.

The product of the milling step may be added to surface coating binders dissolved or dispersed in water, solvent or mixtures of the two, to prepare a surface coating, such as an ink or paint. The reaction of certain metal flake pigments, notably aluminium, is, however unpredictable. Where such a surface coating contains a proportion of water, there exists the possibility that reactions may occur during storage, with the formation of hydrogen gas with the aforementioned hazards. It is therefore desirable to passivate the metal flake during its preparation, through the addition of one or more corrosion inhibiting agents to the milling system.

The milling fluid of the present invention should comply with the following highly desirable requirements, plus as many desirable characteristics as possible.

5 Highly desirable requirements are that the milling fluid is:-

- of low viscosity; < 100cP, preferably < 10 cP , most preferably < 3 cP, at 25°C.
- liquid in the temperature range of 10-40°C normally encountered in metal pigment manufacture,
- 10 • chemically unreactive with the metal pigment being prepared, This could eliminate halogen groups, which may react violently with certain metals in finely divided form, unless in the presence of a corrosion inhibitor.
- of low odour,
- 15 • of low toxicity,
- of low vapour pressure, ideally below 3mm Hg at 25°C and preferably below 0.5 mm Hg at 25°C. This characteristic limits losses to atmosphere through evaporation and helps to prevent the resulting aggregation of the paste product.

20

Desirable characteristics of the milling fluid include:-

- optical transparency,
- zero odour,
- 25 • non-flammability,
- non-classification for supply and transport by the EU and other jurisdictions.

Milling liquids suitable for the process of the invention are low-medium molecular weight alcohols, glycols, ethers and esters, plus certain ketonic species and hetero atom-containing compounds.

Amongst alcohols there may be mentioned pentyl and hexyl alcohols, 2(2-n-butoxy ethoxy ethanol), tetrahydropyran and tetrahydropyran-2-methanol, whilst glycols may comprise, amongst others, ethylene glycol, dimethylene glycol,  
5 diethylene glycol, trimethylene glycol, triethylene glycol, propylene glycols, butylene glycols and glycerol.

Gamma butyrolactone, 2-pyrrolidone, N-methyl pyrrolidone, isophorone, triacetin, 2,5-hexanedione, tetraethylene pentamine, triethyl phosphate, ethyl acetoacetate  
10 and n-methyl formamide may have utility in some systems. Propylene carbonate is also suitable.

Also suitable for the process of the invention are the lower mono and dialkyl ethers, esters and mixed ether esters of mono-, di- and tri- ethylene and propylene glycols. Examples of ethers are ethylene glycol monobutyl ether, diethylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, triethylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, diethylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, triethylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, propylene glycol monobutyl ether,  
20 dipropylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, tripropylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, dipropylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, and tripropylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers. Diamyl ether may also be used.  
25

Examples of esters and mixed ether esters are methoxypropyl acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, dipropylene glycol monomethyl ether acetate and propylene glycol  
30 diacetate. Methyl, ethyl and propyl lactate plus the monomethyl, monoethyl,

dimethyl and diethyl esters of succinic, glutaric and adipic acids may also be used.

Mixtures of any of the above milling liquids may be used.

5

Aforementioned compounds displaying low nominal water solubility may yet be suitable in water-based application systems because they may act as bridging solvents where there is also some water-miscible organic solvent present in the formulation.

10

Particularly preferred are propylene carbonate, dipropylene glycol dimethyl ether, commercially available as Dow Proglyde DMM, (Dow Proglyde DMM is a trademark of the Dow Chemical Company), diethylene glycol monoethyl ether acetate, sold as DE Acetate (Eastman DE acetate is a trade name of the Eastman Chemical Company), tripropylene glycol methyl ether, sold as Dowanol TPM, (Dowanol TPM is a trade name of the Dow Chemical Company), diethylene glycol monobutyl ether acetate, sold by Union Carbide Corporation as butyl Carbitol acetate, (Carbitol is a trademark of the Union Carbide Corporation), a mixture of dimethyl esters of adipic, glutaric and succinic acids, supplied by DuPont under the trade name DBE.

Metals suitable for the performance of the invention include all those metals commercially employed as flake pigments, such as aluminium, zinc, copper, tin, nickel, iron and alloys thereof, such as gold bronze, an alloy of copper and zinc, or stainless steel, an alloy composed mainly of iron. Aluminium and gold bronze are preferred, as they have the greatest commercial potential. There is no criticality to the particle size of the milled flakes, but a median flake diameter range of 6 $\mu\text{m}$  to 600 $\mu\text{m}$ , preferably 10 $\mu\text{m}$  to 300 $\mu\text{m}$ , is generally suitable.

30 Although not essential to the performance of the invention, it is desirable to include corrosion inhibitors in the comminution of the more chemically reactive

metals, such as aluminium. Any compounds capable of inhibiting the reaction of the metal with water may be employed as corrosion inhibitors. Examples are phosphorus-, chromium-, vanadium-, titanium- or silicon-containing compounds. They may be used individually or in admixture.

5

Suitable phosphorus compounds may be organic or inorganic. Simple inorganic phosphates, such as calcium or magnesium phosphate, or more complex phosphosilicate compounds may be used. The latter include calcium phosphosilicate, calcium strontium phosphosilicate and aluminium zirconium zinc phosphosilicate. An especially preferred member of this class is calcium strontium zinc phosphosilicate.

Organic phosphorus compounds include alkyl and dialkyl phosphates, phosphites and their derivatives. Such alkyl and dialkyl groups may contain 1-20 carbon atoms. Iso-octyl acid phosphate may be particularly mentioned. Also especially suitable are phosphate esters of long chain ethoxylated alcohols. Preferred amongst these is Briphos S2D, a product of Rhodia. Briphos S2D is a Rhodia trademark for a phosphated ester of ethoxylated C<sub>12</sub> to C<sub>15</sub> alcohols.

20 Silicon containing compounds capable of inhibiting the reaction of metals with water include organic silanes and silicates, especially tetra ethyl silicate and inorganic silicon compounds such as potassium silicate.

Compounds of molybdenum, vanadium, titanium and tungsten, especially some ammonium salts, have also shown particular suitability in the process of the invention.

Chromium compounds that may be employed in the invention include ammonium dichromate and chromic acid. In this class, the former is preferred as it is less aggressive towards metal grinding media.

Amongst the above corrosion inhibiting compounds, non-resinous organic or inorganic phosphates are especially preferred. They generally offer a high level of corrosion resistance, with few health and safety concerns.

5 Long chain fatty acids, especially stearic and oleic acids, have traditionally been used as lubricants in the conventional hydrocarbon solvent-based milling process. Such lubricants are generally added at a few percent by weight, calculated on the metal weight. They have the effect of preventing cold welding of incipient metal flakes under the action of the milling media. It is an advantage of  
10 the present invention that certain milling liquids do not require the addition of a lubricant. Where there is advantage in their use, lubricants suitable for the process of the invention are generally organic compounds recognised in the art as having both lubrication properties and imparting corrosion resistance and/or adhesion properties. Examples of compounds recognised for good corrosion  
15 resistance properties are phosphate esters of long chain ethoxylated alcohols, lauryl phosphonic acid, and lauryl phosphate. Amongst those compounds imparting particularly good adhesion properties are mineral oils, also known as white oils, which are hydrocarbons having boiling points in the range of 180 to 300°C.

20 The corrosion inhibitor and milling lubricant functions may be advantageously provided by a single chemical substance, for example a substituted phosphate ester such as Briphos S2D, or the functions may be provided by two or more different materials. Such compounds may also improve adhesion to the substrate  
25 when the products of the invention are used in coating applications.

There is no criticality to the mechanism of milling. Any comminution process known in the art for metal flake production may be employed, providing the mechanical energy imparted is not so severe as to damage the metal flakes  
30 being formed. Ball milling is a widely operated process.

Neither is there any criticality to the grinding media, providing they do not undergo undesirable chemical reactions with the other components during or after the comminution stage of the process. Steel and high-density ceramic grinding media are generally satisfactory.

5

Unwanted oversize or undersize metal flake particles may be removed by any suitable means, such as screening of the milled slurry, optionally diluted by more milling liquid. The metal pigment slurry can then be concentrated to a paste by any convenient means, such as a filter press, ready for sale as a paste.

10 Alternatively, it may be admixed with organic binder medium and formed into granules.

Organic binder media include those organic materials habitually employed as binders in paints and inks or as plastics masterbatch carriers. The organic binder 15 chosen is dependent on the envisaged end use of the product of the invention. If the derived granules are to be capable of use in both water-based and solvent-based application systems, the organic binder should be compatible with both systems. Many acrylic and related resins are solvent soluble, but become water soluble on neutralisation with a suitable amine.

20

Alternatively, if desired, the organic binder medium may specifically be a solvent-soluble resin. As examples of such media there may be mentioned cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) resins, coumarone indene, epoxy esters, epoxide melamine and epoxide phenolic 25 condensates, ketone, aldehyde, maleic and phenolic resins and also rosin, cellulose and petroleum derived resins, together with thermoplastic polymers, such as polyacrylates, polyolefins, polyvinyls, styrenics, polyamides, polyesters and copolymers thereof. Also suitable are natural and synthetic waxes, such as montan and paraffin wax and synthetic waxes such as polyethylene and 30 polypropylene waxes.

Where it is desired to introduce liquid organic binders, such as plasticisers, for example to improve application properties, they are desirably added in minor proportions in combination with solid resins, to retain structural rigidity in the resulting granules. Such plasticisers include mineral oils as well as phthalates such as dioctyl or di-isodecyl phthalate, and adipates, such as dioctyl adipate.

5

Amongst organic binders suitable for water-based application systems, gelatin and carrageenen may be mentioned. Some surfactants may also be used, though care must be taken that the adhesion of derived coatings to the substrate

10 is not impaired.

It is an advantage of the granule-forming stage of the process that it is not generally necessary to pre-dissolve or pre-disperse organic binders in solvent. Indeed it may be undesirable to do so, as the viscosity may be reduced too much 15 to provide granules of satisfactory structural rigidity. Rather, dry organic binder may be added to the metal pigment paste, heating if necessary to achieve a homogenous mass, capable of formation into granules without substantial removal of the milling fluid.

20

Granular products of the invention are typically in a form such as tablet, pellet, granule, flake or spherical bead, which provides the attributes of ease of handling, non-dusting and meterability. Granules having a length of 5 to 20mm, and a thickness of 1.5 to 3mm are preferred, as they have been found to offer optimum handling characteristics, especially in plastics applications where it is important to prevent stratification of polymer pellets and the particularly dense 25 products of the invention. Apparatus used for the preparation of such physical forms is well known to those skilled in the art and is described in, for example, European Patent 0134676.

30

The function of the organic binder medium is to bind the metal pigment flakes together to prevent them becoming airborne as dust. Where the organic binder

medium is soluble or dispersible in the milling fluid, it may be added as a concentrated solution or dispersion. Where it is insoluble in the milling fluid, it may be preferable to micronise the binder, that is to say, reduce its particle size to the micron size range. In this latter case, the coherent paste of metal pigment,

5      milling fluid and micronised organic binder medium is formed into particles, for example by mixing and extrusion, then heat treated at elevated temperature, for example 100 to 130°C for a short time, to fuse together the micronised organic binder medium and the metal flake pigment. This process is particularly suited to products for the plastics market, in which suitable organic binder media may be

10     insoluble in the milling liquid. It provides a final product form that has excellent colouristic and application properties when used in the injection moulding or extrusion of thermoplastics.

The invention is further illustrated by the following Examples in which all parts  
15    and percentages are by weight, unless otherwise stated.

#### EXAMPLE 1

20    The following materials were added to a rigid cylindrical polypropylene container of volume one litre :

- 1607g of 3mm diameter stainless steel balls
- 206.8g of butyl Carbitol acetate
- 25.   30g of aluminium powder of approximately 7µm median particle diameter
- 2.089g of oleic acid

The sealed container and contents were put on a vibratory mill. After three hours, the mill contents were removed and separated from the steel balls by sieving,  
30    prior to recovery by vacuum filtration using a Buchner funnel. The aluminium pigment flakes produced were then incorporated into both a solvent based and a

water based acrylic ink system. A bright metallic appearance with good coverage was obtained in both ink systems.

## 5 EXAMPLE 2

The following mixture was milled for three hours in a vibratory mill, sieved and concentrated by vacuum filtration as described in Example 1 :-

- 10 1607g of 3mm diameter stainless steel balls  
206.8g of Proglyde DMM  
30g of a fine aluminium powder of approx. 7 $\mu\text{m}$  median particle diameter  
2.089g of Briphos S2D, which had been neutralised with triethanolamine.
- 15 The resulting pigment flakes were then incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright ink, with a good metallic appearance and good coverage was obtained in both ink systems.

- 20 Corrosion resistance of this aluminium pigment was tested by measuring the gas evolved when formulated in an acrylic coating system, Joncryl 537, and stored for one week at 52°C. (Joncryl 537 is a dispersion of an acrylic copolymer in water. Joncryl is a trademark of S. C. Johnson & Son Inc.) The amount of gas evolved, for 10g of this metallic pigment (as solids) in 150g of Joncryl 537 and 50g of water was 8.6ml This indicated that the aluminium flake surfaces were well protected from reaction with water.
- 25

## EXAMPLE 3

- 30 The following mixture was milled for three hours in a vibratory mill, sieved and concentrated by vacuum filtration as described in Example 1:-

1607g of 3mm diameter stainless steel balls

206.8g of Dowanol TPM

30g of aluminium powder of approx. 7 $\mu\text{m}$  median particle diameter

5

No lubricant was added to this mill formulation. The aluminium pigment flakes produced were incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright metallic ink, with good coverage was obtained in both systems.

10

#### **EXAMPLE 4**

The following mixture was milled for three hours in a vibratory mill, sieved and

15 concentrated by vacuum filtration as described in Example 1:-

1607g of 3mm diameter stainless steel balls

206.8g of Eastman DE acetate

30g of aluminium powder of approximately 7 $\mu\text{m}$  median particle diameter

20 2.089g of stearic acid

The aluminium pigment flakes produced were incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright ink, with good coverage was obtained in both ink systems.

25

#### **EXAMPLE 5**

The following mixture was milled for three hours in a vibratory mill, sieved and

30 concentrated by vacuum filtration as described in Example 1:-

1607g of 3mm diameter stainless steel balls

206.8g of butyl Carbitol acetate

30g of aluminium powder of approximately 7 $\mu\text{m}$  median particle diameter

2.089g of mineral oil

5

Mineral oil is a saturated hydrocarbon of low volatility, having a vapour pressure of approximately 0.001mm Hg.

10 The aluminium pigment flakes produced were incorporated into both solvent based and water based acrylic ink systems and drawn down on card using a wire-wound bar. A bright metallic appearance ink, with a good coverage and good adhesion on a tape removal test was obtained in both ink systems.

15 **EXAMPLE 6**

The following mixture was milled for three hours in a vibratory mill, sieved and followed by pigment concentration by vacuum filtration as described in Example

1:-

20

1607g of 3mm diameter stainless steel balls

206.8g of DuPont DBE

30g of aluminium powder of approximately 7 $\mu\text{m}$  median particle diameter

2.089g of oleic acid

25

The aluminium pigment flakes produced were incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright metallic ink, with good coverage and good adhesion on a tape removal test was obtained in both ink systems.

30

## **EXAMPLE 7**

The following mixture was milled for five hours in a vibratory mill, sieved and followed by pigment concentration by vacuum filtration as described in Example

5 1:-

1607g of 3mm diameter stainless steel balls

206.8g of Dowanol Proglyde DMM

60g of copper powder

10 2.089g of stearic acid

The resultant copper pigment flakes produced were then incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright copper coloured ink effect was obtained with both ink systems.

15

## **EXAMPLE 8**

The following mixture was milled in a vibratory mill for five hours, sieved and

20 followed by pigment concentration by vacuum filtration. As in Example 1:-

1607g of 3mm diameter stainless steel balls

206.8g of Dowanol Proglyde DMM

60g of iron powder of approximate median diameter of 16 $\mu\text{m}$

25 2.089g of oleic acid

The resultant pigment flakes produced were then incorporated into both a solvent based and a water based ink system. A metallic, gunmetal colour effect was obtained with both ink systems.

30

## **EXAMPLE 9**

The following mixture was milled in a vibratory mill, sieved and concentrated by vacuum filtration as described in Example 1 :-

5

1607g of 3mm diameter stainless steel balls

206.8g of Dowanol TPM

30g of aluminium powder of median particle size of approximately 7 µm

2.089g of lauryl phosphate

10

The aluminium pigment flakes produced were then incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright metallic effect ink, with good coverage was obtained in the water based system.

15

## **EXAMPLE 10**

The following mixture was milled in a vibratory mill, sieved and concentrated by vacuum filtration, as described in Example 1 :-

20

1607g of 3mm diameter stainless steel balls

206.8g of Eastman DE Acetate

30g of aluminium powder of median particle size of approximately 7µm

2.089g of octadecyl phosphonic acid

25

The aluminium pigment flakes produced were incorporated into both a solvent based and a water based ink system and drawn down. A bright metallic appearance ink, with good coverage was obtained in both systems.

30

### **EXAMPLE 11**

The following mixture was milled in a vibratory mill sieved and concentrated by vacuum filtration as described in Example 1:-

5

1607g of 3mm diameter stainless steel balls

206.8g of Dupont DBE

30g of aluminium powder of median particle size of approximately 7 $\mu\text{m}$

2.089g of lauryl phosphonic acid

10

Lauryl phosphonic acid was supplied by Rhodia.

The aluminium pigment flakes produced were incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright ink, with

15 good coverage was obtained in both systems.

### **EXAMPLE 12**

20 The following mixture was milled in a vibratory mill, sieved and concentrated by vacuum filtration, as described in Example 1:-

1607g of 3mm diameter stainless steel balls

206.8g of propylene carbonate

25 30g of aluminium powder of median particle size of approximately 7 $\mu\text{m}$

2.089g of oleic acid

The aluminium pigment flakes produced were incorporated into both a solvent based and a water based acrylic ink system and drawn down. A bright metallic

30 appearance ink, with good coverage was obtained in both systems.

### **EXAMPLE 13**

5 The following mixture was milled for ten hours in a sealed, cylindrical pot of 30cm diameter, set on revolving rollers. The resulting slurry was sieved and concentrated by vacuum filtration as described in Example 1:-

- 3330g of 3mm diameter stainless steel balls
- 428.5g of Eastman DE acetate
- 10 62.2g of aluminium powder of approximately 7 $\mu\text{m}$  median particle diameter.

15 35.4g of this paste product, containing 20g of aluminium metal, was added to 5.0g Laropal A81 resin (BASF GmbH) and the mixture heated to 75°C for 30 minutes, with gentle stirring to provide a homogenous mixture. The mixture was forced through a perforated mesh to give granules of approx. 10mm length and 2mm thickness.

20 The resultant granules were dispersed in an ethyl acetate-based acrylic ink system by slow speed paddle stirring, then drawn down against the feed paste, similarly dispersed. The drawdown showed that the granulated material was very similar in appearance to the feed paste. The physical form of the granule made it more easily handled than the paste.

### **25 EXAMPLE 14**

The following mixture was milled in a vibratory mill for 6 hours, sieved and concentrated by vacuum filtration as described in Example 1:-

- 30 1607g of 3mm diameter stainless steel balls
- 206.8g of Eastman DE acetate

30g of aluminium powder of median particle size of approximately 7 µm  
2.089g of oleic acid

15.2g of the thus formed aluminium paste, containing 10g of aluminium metal,  
5 was added to 3.2g low molecular weight polyethylene wax granules and the mixture heated at 100°C for 1 hour whilst gently mixing to provide a homogenous mixture. The mixture was granulated and recovered as described in Example 13.

10 The resultant granules were incorporated at 1.0% by weight in polypropylene in an injection-moulding machine held at approximately 220°C. The moulded articles exhibited a smooth, uniformly pigmented, silver surface, with no obvious defects. The granule had a consistency that was more easily handled than the feed paste.

CLAIMS

1. Process for producing a low volatility metal flake pigment composition, which comprises milling metal powder in a non-aqueous, non-hydrocarbon low volatility milling fluid.  
5
2. Process according to claim 1, which further comprises the addition of one or more substances that act as a lubricant and/or corrosion inhibitor.
- 10 3. Process according to claim 1 or claim 2, which further comprises the step of removing oversize or undersize particles after milling.
4. Process according to any of the preceding claims, which further comprises concentrating after milling to a metal flake pigment paste of 50-  
15 90% metal by weight.
5. Process according to claim 4, wherein the paste is converted to a granule form by incorporating an organic binder to form a coherent paste of organic binder, milling fluid and metal flake pigment.  
20
6. Process according to claim 5, wherein the paste of organic binder, milling fluid and metal flake pigment is in a particulate form such that at least 98% by weight of the particles are retained on a sieve having a 150µm aperture.  
25
7. Process according to claim 5 or claim 6, wherein the granules have a length of 5 to 20mm and a thickness of 1.5 to 3mm.
8. Process according to any of the preceding claims, which further comprises a step of treating the milled metal flakes in the milling fluid.  
30

9. Process according to claim 8, wherein the metal flakes are treated with ammonium dichromate or ammonium or potassium permanganate or coated with silica or alumina.

5        10. Process according to any of the preceding claims, wherein the milling fluid is pentyl alcohol, hexyl alcohol, 2(2-n-butoxy ethoxy ethanol), tetrahydropyran, tetrahydropyran-2-methanol, ethylene glycol, dimethylene glycol, diethylene glycol, trimethylene glycol, triethylene glycol, propylene glycols, butylene glycols, glycerol, gamma butyrolactone, 2-pyrrolidone, N-methyl pyrrolidone, isophorone, triacetin, 2,5-hexanedione, tetraethylene pentamine, triethyl phosphate, ethyl acetoacetate, n-methyl formamide, propylene carbonate, ethylene glycol monobutyl ether, diethylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, triethylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, diethylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, triethylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, propylene glycol monobutyl ether, dipropylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, tripropylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers, dipropylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, tripropylene glycol dimethyl, diethyl, dipropyl and dibutyl ethers, diamyl ether, methoxypropyl acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, dipropylene glycol monomethyl ether acetate, propylene glycol diacetate, methyl, ethyl and propyl lactate or the monomethyl, monoethyl, dimethyl and diethyl esters of succinic, glutaric and adipic acids, or a mixture of any two or more of these.

11. Process according to claim 10, wherein the milling fluid is propylene carbonate, tripropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol

monobutyl ether acetate, or mixtures of dimethyl esters of adipic, glutaric and succinic acids.

12. Process according to any of the preceding claims, wherein the metal is  
5 aluminium, zinc, copper, tin, nickel, iron, stainless steel or an alloy thereof.

13. Process according to claim 11, wherein the metal is aluminium or gold  
bronze.

10 14. Process according to any of the preceding claims, wherein the metal  
pigment particles have a median diameter of 6 $\mu$ m to 600 $\mu$ m..

15. Process according to claim 13, wherein the metal pigment particles  
have a median diameter of 10 $\mu$ m to 300 $\mu$ m.

15  
16. Process according to any of claims 2 to 15, wherein the corrosion  
inhibitor is calcium phosphate, magnesium phosphate, calcium phosphosilicate,  
calcium strontium phosphosilicate, aluminium zirconium zinc phosphosilicate,  
calcium strontium zinc phosphosilicate, alkyl and dialkyl phosphates, phosphites  
20 and their derivatives, phosphate esters of long chain ethoxylated alcohols,  
organic silanes and silicates, ammonium salts of molybdenum, vanadium,  
titanium and tungsten, ammonium dichromate or chromic acid.

17. Process according to any of claims 2 to 16, wherein the lubricant is a  
25 long chain fatty acid, a phosphate ester of a long chain ethoxylated alcohol, lauryl  
phosphonic acid, lauryl phosphate or mineral oils which are hydrocarbons having  
boiling ranges from 180 to 300°C.

18. Process according to any of the preceding claims, comprising ball  
30 milling the metal powder.

19. Use of a non-aqueous, non-hydrocarbon milling fluid in a process of milling a metal powder as claimed in any of the preceding claims.
20. A metal pigment paste obtainable by the process of any of claims 1 to 18.  
5
21. A metal pigment paste produced by the process of any of claims 1 to 18.
22. A granule obtainable by the process of any of claims 5 to 18.  
10
23. A granule produced by the process of any of claims 5 to 18.
24. An ink or surface coating comprising the metal pigment paste or granules produced by a process according to any of claims 1 to 18 and adding to surface coating binders dissolved or dispersed in water, solvent or mixtures of the two.  
15
25. Article obtainable by shaping a composition comprising granules produced by the process of any of claims 5 to 18.  
20
26. Article obtainable by injection moulding or by extrusion of a thermoplastic, comprising granules produced by the process of any of claims 5 to 18
27. Shaped article comprising a thermoplastic or thermosetting polymer and granules produced by the process of any of claims 5 to 18.  
25